Surface characterization of Ti-Si-C-ON coatings for orthopedic devices: XPS and Raman spectroscopy

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1. Introduction

In recent years, strong efforts have been made on the development of new coatings for orthopedic implants, in order to improve their tribological properties as well as their biocompatibility. The aim has been guided towards reducing failures due to overloading, fatigue, wear, corrosion and infection\cite{1,2}. Titanium nitride (TiN), for instance, has been used for biomedical applications. However, it is reported that high oxygen content could lead to taylor the material to a much wider set of desired properties. On the other hand, it is reported that high oxygen content could lead to low hardness of the films\cite{8}. Nevertheless, the influence of oxygen on the structure of the quaternary compound Ti-Si-C-N is not well established yet.

Despite the results already obtained, there is still a lack in the knowledge of the structural arrangements of these coatings. Hence, this paper reports the chemical bonding information obtained by Raman and X-ray Photoelectron Spectroscopy (XPS). Since the biological properties are important to investigate the feasibility of these Ti-Si-C-ON coatings for orthopedic applications, additional biological results are also presented.

2. Experimental details

The Ti-Si-C-ON samples were deposited by d.c. reactive magnetron sputtering from two opposed high purity (99.6\%) Ti...
targets (20 × 10 cm²): one Ti target with incrusted Si pellets (hereafter designated as TiC target) and the other with carbon pellets (designated as TiSi target), placed in the preferential eroded zone. The area occupied by the pellets was close to 11 cm² in each target. Depositions were carried out under an Ar + (N₂ + O₂) atmosphere on an Alcatel SCM 650 sputtering system. The base pressure in the chamber was about 10⁻⁴ Pa and rose to 4 × 10⁻¹ Pa during the depositions. The coatings were deposited on 316L stainless steel (medical grade steel) and on single crystal silicon (100) substrates for further structural analysis. During the depositions, the substrates were rotated 70 mm above the target at a constant speed of 7 rpm to assure a homogenous deposition of the films.

In order to change the oxygen content, samples were grown using different N₂ + O₂ flow rates (ranging N₂ from 6.5 to 0 sccm and O₂ from 0 to 5.25 sccm), while maintaining an Ar flow constant at 60 sccm. The substrate bias voltage and the temperature were kept constant at −50 V and 200 °C, respectively. The current density applied to the TiC target was 5 mA/cm² and to the TiSi target was 6 mA/cm². The detailed information about the deposition parameters is presented on Table 1.

The stoichiometry of the films was investigated by means of Rutherford Backscattering Spectrometry (RBS) and Glow Discharge Optical Emission Spectroscopy (GDOES). RBS experiments were performed with a 5 MV HVEE Tandetron [13]. RBS spectra were collected using 2 MeV H⁺ ions at an ion dose of 7 μC. Data acquisition was performed simultaneously using two silicon surface barrier detectors located at scattering angles of 170° and 135°, respectively, and with an energy resolution of 15 keV. The experimental spectra were fitted with the program RBX [14]. GDOES was carried out using a Jobin Yvon RF GD Profiler equipped with a 4 mm diameter anode and operating at a typical radio frequency discharge pressure of 650 Pa and power of 40 W. The setup was calibrated using standard materials of known composition. In order to improve the quantification of nitrogen, a series of chromium nitride coatings, deposited by magnetron sputtering, were used as calibration samples [15].

Chemical bonding information was obtained by Raman and X-ray Photoelectron Spectroscopy (XPS). The Raman spectra were acquired with a Jobin Yvon HR 460 monochromator and a nitrogen cooled CCD. The excitation light was the 514.5 nm line of an Ar-Kr laser. The incident and scattered beams were focused using an Olympus microscope and a Kaiser Super-Notch laser. The incident and scattered beams were focused using an Olympus microscope and a Kaiser Super-Notch laser. The XPS spectra were measured using a hemispherical analyzer (SPECs Phoibos 100 MCD-5). The pass energy was 9 eV giving a constant resolution of 0.9 eV. The Au 4f/2, Ag 3d/2 and Cu 2p/3/2 lines of standard samples at 84.0, 368.3 and 932.7 eV, respectively, were used in order to calibrate binding energies. A twin anode (Mg and Al) X-ray source was operated at a constant power of 300 W using Mg Kα radiation. The samples were sputter-cleaned in situ using a broad 3 keV Ar⁺ beam, for 10 min.

For the biological studies (biofilm formation and cytotoxicity) one sample per regime was assayed, namely samples with N/Ti of 0.04, 0.77 and 2.11. Biofilms of *Staphylococcus epidermidis* were formed, in Tryptic Soy Broth, on coated materials for 48 h, at 120 rpm and 37 °C. Total biomass was determined by staining samples with crystal violet (Abs CV) and by absorbance reading at 570 nm [16]. At least three replicates were performed in three different assays. Cytotoxicity was determined using a fibroblast 3T3 cell line. Coupons of sample materials were placed in indirect contact (an inert plastic holder was used) with confluent cells, for 24 h at 37 °C and 5% CO₂ in 1 ml of Dulbecco’s Modified Eagle Medium (supplemented with 10% of fetal bovine serum) and the controls were performed in the absence of coupons. Cellular activity was determined using MTS (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium, inner salt - Promega CellTiter 96AQT™ Non-Radioactive Cell Proliferation Assay). The percentage of cell death was determined in relation to the control, which was considered 100% of cellular activity. Again, three replicates were performed in, at least, three different assays.

3. Results and discussion

3.1. Chemical composition

The atomic composition of the samples deposited on silicon substrates, determined by RBS and GDOES, is given in Table 1. It should be pointed out that the results of the chemical composition of the films deposited on the 316L steel, obtained by these two techniques, do not show significant differences from the ones of Table 1. The values of an average of the RBS and GDOES analyses, as a function of the oxygen partial pressure and the nitrogen partial pressure ratio (pO₂/pN₂), are also shown in Table 1. The N/Ti atomic ratio tends to decrease with increasing pO₂/pN₂ and the oxygen content shows an opposite behavior. Taking into account the different elemental compositions, 3 different regimes, based on the samples concentrations, can be observed: (I) N/Ti = 2.11 (high atomic ratio) and low oxygen content; (II) 0.77 < N/Ti < 1.86 (intermediate atomic ratio) and (III) N/Ti < 0.12 (low ratio) and high oxygen content. The chemical composition of the films as a function of deposition process parameters (pO₂/pN₂) and these different regimes are in agreement with results already published [12]. As such, we will use here the referred regimes, for consistency with the previously reported results.

In Fig. 1 GDOES depth profiles are shown for coatings belonging to regime I (Fig. 1a) and III (Fig. 1b), deposited on steel substrates. Despite some carbon and oxygen contamination in the near surface, the elemental composition (Ti, Si, C, O and N) of the films, along their depth, is homogeneous, for both regimes. For the sample in regime I, the intermediate adhesive titanium-silicon layer is clearly observed.

3.2. X-ray diffraction results

Previously, the X-ray diffraction (XRD) results for these samples were already presented and discussed [12]. Nevertheless, for the sake of clarity some features should be pointed out. The XRD patterns from the samples within regime I, (high N/Ti atomic ratio)
3.3. Raman and XPS analysis

The structural and chemical properties of the Ti–Si–C–ON films were probed by means of Raman and XPS studies. Fig. 2 shows the Raman spectra of Ti–Si–C–ON samples deposited on silicon, with different \( \frac{p_{O_2}}{p_{N_2}} \) and consequently different regimes for the N/Ti atomic ratio. The absence of sharp and well-defined peaks suggests local structural disorder of the prepared films. In a perfect crystal with fcc structure (as in TiN) every ion is at a site of inversion symmetry and the first-order Raman scattering is forbidden [17]. However, Physical Vapor Deposition (PVD) coatings are known to exhibit reflections that correspond to a mixture of two different phases: a metallic-like Ti and an fcc TiN type structure. For regime (II) \( 0.77 < \frac{N}{Ti} < 1.86 \) (intermediate atomic ratio), the films crystallize also in a B1-NaCl crystal structure typical for TiCo$_2$N$_{0.8}$. For regime III–N/Ti < 0.12 (low ratio) and high oxygen content, the films exhibit a polycrystalline structure, due to the increase of the oxygen concentration. The increasing concentration of N-vacancies (decreasing N/Ti) can progressively be filled by oxygen atoms, forming Ti-O phases. These different regimes and the corresponding phases were obtained for films deposited on both substrates.

For Ti–Si–N–O films a silicon content of 10 at % induced a nearly nanocrystalline structure of TiSiN(O) with small average grain size: 1.5–2 nm. In the present case, the presence of Si–C–N bonds in the XPS spectrum indicates that silicon is partially dissolved in the films forming a Ti-Si-(C,N) cubic solid. Within the O1s region it is observed a weak and wide peak (FWHM > 3 eV) centered at 531.2 eV. This binding energy lies between the reported values for crystal lattice O-Ti (529.6 eV) and O-Si (532.7 eV) bonds, suggesting the formation of titanium silicates [24,25].

For regime (II) \( 0.77 < \frac{N}{Ti} < 1.86 \) (intermediate atomic ratio), both a decrease in nitrogen content and an increase in carbon content were observed. The Raman spectrum for the sample with N/Ti = 1.86 shows the same peaks as the one for the sample of regime I, but a shoulder located at around 720 cm$^{-1}$ starts to appear. This band, also observed in CN$_x$ films [26], can be attributed to the Ti(C,N) phase. In the XPS spectra there is a progressive decrease of the Ti-N signal (Fig. 3e) and a subsequent increase of the C-Ti bonds (Fig. 3c), which is consistent with the progressive substitution of the nitrogen by carbon, on the underlying TiN structure, to form a fcc Ti(C,N) phase. The Si2p XPS spectrum of sample with N/Ti = 1.86 shows a major contribution at 102 eV attributed to Si-N bonds [22] that can be associated to an amorphous Si$_x$N$_y$ phase. This phase practically disappears on sample with N/Ti = 0.77 due to the decrease of nitrogen in the deposition chamber.

For Ti–Si–C–ON films belonging to (left) regime I: N/Ti = 2.11 \( \frac{p_{O_2}}{p_{N_2}} = 0.046 \) and (right) regime III: N/Ti = 0.04 \( \frac{p_{O_2}}{p_{N_2}} = 20 \).
A considerable modification of the spectral shape occurs for the samples deposited with high $p_{O_2}/p_{N_2}$ that induces a low N/Ti atomic ratio and high oxygen content (regime III N/Ti $\leq 0.12$). The Raman spectrum for the sample with N/Ti $= 0.12$ confirms the progressive nitrogen substitution by carbon atoms to form fcc Ti (C,N) phases, since the band around $720 \text{ cm}^{-1}$, due to the C-N bond vibration, is clearly visible. This is supported by the shift of the Ti2p main signal towards lower binding energies (indicating the formation of a Ti-C-N phase as discussed in [24]) and the increase of the C-Ti bonds observed in the XPS spectra of Fig. 3a and c, respectively. The Si2p spectrum only shows a small contribution of metallic silicon at 99 eV, as the amount of nitrogen present in the films ($7\%$) is too low to form a SiN$_x$ phase in sample with N/Ti $= 0.77$. Finally, for the sample with higher O content (N/Ti $= 0.04$ atomic ratio), the Raman spectrum clearly shows the presence of bands characteristic of the rutile phase of TiO$_2$ [18]. It is worth noting that these bands are quite broad, due to structural disorder or stress in this phase, but also due to nanometric grain sizes present in the films. Similarly, the observed Raman band around $1030 \text{ cm}^{-1}$ is due to the stretching Si-O vibration from SiO$_x$ [27]. These results agree with the previous XRD and FTIR characterizations [12], since, the sample deposited with high $p_{O_2}/p_{N_2}$ low N/Ti atomic ratio and high oxygen content (regime N/Ti $\leq 0.12$), exhibits a polycrystalline structure with the formation of nanosized clusters. The XPS Ti2p spectrum presents a doublet at 459 eV and at $464.8 \text{ eV}$ corresponding to titanium oxide [28] bonds. Moreover, the Si2p spectrum has a distinctive peak near $103.2 \text{ eV}$ associated to Si-O bonds [29]. This is supported by the broad peak ($> 2 \text{ eV}$) of O1s centered at $532.4 \text{ eV}$ that can be deconvoluted into two components at $532.7 \text{ eV}$ and $531.4 \text{ eV}$, respectively. The first component should be attributed to O-Si bonds and the second one suggests the formation of Ti-O-Si cross-linking bonds by analogy with similar results found during the oxidation of Ti/Al interfaces [28]. The very low nitrogen content in this sample (see Fig. 3e) confirms that the predominant phases are titanium and silicon oxides, in agreement with the Raman results.

Fig. 3. XPS spectra of a) Ti2p, b) C1s, c) N1s, d) O1s and e) Si 2p core levels of the Ti–Si–C–ON coatings deposited by DC reactive magnetron sputtering, with different N/Ti ratios.
3.4. Biological characterization

Microbial colonization of implant devices has been one of the main causes of implant failure and this colonization is often associated with biofilm formation. In these biofilms, heterogeneous communities of microorganisms are embedded in a polymeric matrix, which confers them resistance to antimicrobial agents and allows them future detachment and colonization/infestation of additional body sites. Moreover, as implants have to be in direct contact with the human body they must be biocompatible, meaning that they cannot cause human tissue cell death. Here, the biological characterization, which includes the determination of biofilm formation and cytotoxicity of the films, was performed with one representative sample from each regime (Fig. 4).

From Fig. 4 it is possible to observe that all assayed samples were prone to microbial colonization. Previously, it was shown that the sample with low N/Ti atomic ratio and high oxygen content (regime III) presented a lower biomass amount than the samples from the two other regimes (which presented similar values among them) due to the formation of titanium oxide rich surfaces that are less prone to colonization. Similar results were also described by other authors [30,31] enhancing the microbial colonization inhibition of titanium dioxide surfaces, even for other applications. However, its cytotoxicity analysis revealed a high value of cellular death, hindering its selection as biomaterial. In fact, both properties should always be assessed because a biomaterial surface must resist biofilm formation as well as presenting low cytotoxicity.

Regarding the cytotoxicity results here presented (circles on Fig. 4) it is possible to verify that the percentage of cell death varies according to the regime of samples preparation. The sample from regime I showed lower cytotoxicity than the samples from the other regimes. That sample is characterized by a TiN structure, in opposition to the sample with a composition more similar to TiO₂ (regime III), which presented a higher value of cytotoxicity. Thus, aiming at determining which coating preparation conditions lead to the best biological properties it is possible to verify that, from all the samples assayed, the film with N/Ti = 2.11, from regime I presented the best compromise (lowest cytotoxicity and a moderate microbial colonization).

4. Conclusions

Ti-Si-C-O thin films have been prepared by unbalanced d.c. magnetron sputtering with different \( p_{O_2}/p_{Ar} \). Their structural and chemical properties were characterized, by Raman and XPS spectroscopy, and correlated with their biofilm formation and cytotoxicity.

From the Raman and XPS analysis, 3 different composition regimes were observed: (I) N/Ti = 2.11 (high atomic ratio) and low oxygen content; (II) 0.77 ≤ N/Ti ≤ 1.86 (intermediate atomic ratio) and (III) N/Ti ≤ 0.12 (low ratio) and high oxygen content. The film composition varied from TiN within the regime I (N/Ti = 2.11), to TiCN within the regime II (0.77 ≤ N/Ti ≤ 1.86), towards titanium oxide on regime III (N/Ti ≤ 0.12).

From the analysis of the biological properties it can be ascertained that there was biofilm formation on all samples and that they all presented low cytotoxicity. However, samples from regime I (high N/Ti ratio) presented moderate biofilm formation and low cytotoxicity.

In conclusion, this work puts on evidence that using different parameters during the coating process leads to different regimes ranging from TiO₂ to TiN, and that the latter represents the best choice for the coating of biomaterials, since it presents the best compromise between biological properties (lowest cytotoxicity and low microbial colonization).

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